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ELEANOR FRANCES SEILER

A.B., University of Denver, 1913
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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS

1922

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY ELEANOR FRANCES SEILER

ENTITLED THE COLOR SENSITIVENESS OF PHOTO-ELECTRIC CELLS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN PHYSICS

Jakob Kunz
In Charge of Thesis

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Head of Department

Recommendation concurred in*

F. R. Watson. E. H. Williams

Chas. T. Knipp.

Committee on Final Examination*

*Required for doctor's degree but not for master's

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COLOR-SENSITIVENESS OF PHOTO-ELECTRIC CELLS

By ELEANOR FRANCES SEILER

ABSTRACT

Color-sensitiveness curves of thirty photo-electric cells, including all the alkali metals and hydrides of Na, K, Rb, and Cs.—As great care was used in mounting the apparatus rigidly, in calibrating the thermo-couple and wave-length scale, and in maintaining a constant source of light, the curves were accurately determined and this enabled the *wave-lengths of maximum sensitiveness* to be located within about 1 $\mu\mu$. It was found that as the atomic weight of the alkali metal increases, the maximum sensitiveness decreases, the resonance peak becomes broader, and λ_{max} shifts toward the red. The author suggests that these changes may be associated with the increase in atomic volume. For glass cells filled with argon at low pressure, λ_{max} was 405, 419, 440, 473, and 539 $\mu\mu$ for Li, Na, K, Rb, and Cs respectively, while for the corresponding hydrides NaH, KH, RbH, and CsH, the values were larger: 427, 456, 481, and 540 $\mu\mu$ respectively. With neon instead of argon, in the case of NaH and KH, λ_{max} was about 20 $\mu\mu$ shorter. And while, in the case of KH, pyrex cells gave the same curve as glass ones, quartz cells showed a longer λ_{max} for both KH and RbH, contrary to what one would expect from differences in absorption. Since the effects of gas and of cell wall were not eliminated and the normal and selective photo-electric effects were not differentiated, the curves are characteristic of the particular cells rather than of the various metals alone; nevertheless it is of interest to note that the products of λ_{max} with (1) resonance potential, (2) ionization potential, and (3) absolute melting temperature of the corresponding metals are each roughly constant. The hydride cells were somewhat more sensitive than the corresponding metal cells.

Fatigue tests of two photo-electric cells. The effect of illuminating a *K cell* for 525 hours was to increase its sensitiveness by about 70 per cent, whereas a *KH cell* remained constant in sensitiveness during 1000 hours' illumination.

Preparation of a lithium photo-electric cell. It was found possible to dissolve lithium in aethylamine if absolutely dry and if a trace of ammonia was present. A uniformly distributed layer of lithium was obtained by evaporating the solution.

Method of preparing pure aethylamine is described.

I. INTRODUCTION

In 1918 T. Shinomiya[1] carried out an experimental determination of the maximum wave-length color-sensitiveness point (λ_{max}) of photo-electric cells of the pure alkali metals sodium, potassium, and rubidium, and of the colloidal modification of the alkali hydrides of these same metals. He found that the λ_{max} was not the same for the pure metal and the hydride, but that a shift occurred, the nature of which was not fully determined.

The object of this investigation was threefold:

1. To obtain more consistent results on the shifting phenomenon and to secure conclusive experimental proof of its direction and amount by the use of many more cells and the extension of the work to include all the alkali metals. No satisfactory theory has been advanced to explain the cause of this shifting of the wave-length of maximum sensitiveness. However, the results of this investigation prove the existence of such a phenomenon, and furthermore they show the shift to be consistently always in the same direction, namely, toward longer wave-lengths when the alkali metals were sensitized by means of hydrogen.

2. To complete the study of the color-sensitiveness for the whole group of alkali metals. When the photo-electric cell is to be used in making photometric measurements, it is necessary to have a complete knowledge of its curve of sensitiveness. In scientific literature it is found that the curves given contain only a few points, which hardly suffice to determine the point of maximum sensitiveness or the general nature of the curves with much accuracy. The ideal photo-electric cell would have the same color-sensitiveness as the human eye.

3. To furnish data for theoretical purposes in the application of the quantum theory to chemistry. No general agreement has yet been reached regarding the relation of the selective to the normal photo-electric effect. Wiedemann[2] found that hydrogen was essential for the selective effect of potassium. The results of this experiment gave a decided selective effect in cells where the potassium was repeatedly distilled in vacuo. According to Millikan

[1] *Astrophysical Journal*, **49**, 303, 1919.

[2] *Berichte der deutschen physikalischen Gesellschaft*, **18**, 333, 1916.

and Souder[1] there is an "essential identity" of the two effects. This investigation was not carried on with the purpose of getting either effect to the elimination of the other. Primary interest was centered in the photometric properties of the cell and not of the alkali metals as such. Apparently there is considerable difference in sensitiveness when the absorption of light through the glass is taken into account and when gas is present in the cells.

II. THE APPARATUS AND METHOD

A. THE CALIBRATIONS

In order to measure the energy of illumination throughout the visible spectrum and the corresponding wave-lengths of light, it was necessary to make four calibrations, about every month during the course of the investigation. We will call these calibrations: (1) thermo-couple, (2) scale-energy, (3) spectrometer, and (4) scale-wave-length.

1. *Thermo-couple.* A thermo-couple, furnished by W. W. Coblentz from the Bureau of Standards, was calibrated by means of the light from a Hefner lamp. Chemically pure amyl acetate was put into the lamp, which was placed exactly one meter from the thermo-couple and in the same horizontal plane with it. Both were placed in a large two-compartment box, which was completely blackened. The partition contained a shutter, by means of which the light could be allowed to fall upon the thermo-couple, and which acted as a partial diaphragm. A hooded chimney was placed above the lamp to take care of the heat from the flame. A small glass window, with a horizontal line on it, was set in the box directly behind the image of the flame, so that the flame could be accurately adjusted to the proper height and observed from the outside. The box being tight and free from air currents, the flame soon came to an equilibrium condition. Two fine wires led from the thermo-couple to an insulating plug in the back of the box. There they were soldered to heavy double silk-wound copper wires, which led through the plug down a heavy-walled wooden tube to a galvanometer. This tube served the purpose of keeping the temperature

[1] *Proceedings of the National Academy of Science*, 2, 19, 1916.

constant and of preventing air currents. The lead wires in the tube were insulated by passing down the center over strips of hard rubber. The galvanometer was a Leeds and Northrup high sensitivity type, whose figure of merit was 2.7×10^{-9}. It was inclosed in a box about which tin foil was wrapped for earthing.

These precautions made the thermo-galvanometer deflections exceedingly steady, and a reading could be repeated time and time again with not as much as 1 per cent of variation. The mean of twenty readings gave a deflection of 121 mm. The energy radiating from a Hefner lamp, according to K. Ångstrom,[1] is 1089 ergs per sec. per sq. cm at a distance of one meter. Hence a deflection of 1 mm corresponded to a flow of energy of 9 ergs per sec. per sq. cm. The slit of the thermo-couple was a trifle narrower than the slit L (Fig. 2) admitting light to the photo-electric cell, so that the former was always covered by light. The area of L was 0.2842 sq. cm, and hence the energy passing through that slit per mm of deflection of the galvanometer of the thermo-couple was $9 \cdot 0.2842$ or 2.558 ergs.

2. *Scale-energy.* The thermo-couple was placed with its slit directly behind L and held there rigidly. It was connected to the same galvanometer through another tube, which was completely wrapped with tin foil and earthed.

By means of a fine screw R (Fig. 2), the thermo-couple was moved along the millimeter scale S through the entire spectrum, and the mean of three readings taken as the deflection at each point. Then by plotting a curve with scale-readings as abscissae and energy in ergs as ordinates, the energy incident upon every point in the spectrum was exactly determined.

3. *Spectrometer.* Since the Hilger constant-deviation spectrometer was to be used in determining the wave-length incident at every corresponding point on the scale S, it, too, had to be calibrated. This was done by means of a Plücker discharge tube. The prism of the spectrometer was adjusted so that the corrections were very slight.

4. *Scale-wave-length.* The wave-lengths corresponding to the points along the scale were then obtained with this instrument.

[1] W. W. Coblentz, *Bulletin of Bureau of Standards*, 11, 95, 1914.

The lines seen in the spectrometer were almost as fine as those seen when the discharge tube was used, showing that the light was very nearly monochromatic. They became somewhat broader toward the red end of the spectrum, but this was unavoidable and, as the experiment did not require great accuracy in that region, accuracy was sacrificed to get better definition in the other end of the spectrum. By plotting a curve with wave-lengths as abscissae and scale-readings as ordinates, the wave-length corresponding to any position on the scale was obtained.

B. THE EXPERIMENT

1. *The optical system.* The optical system used in this investigation was an improvement over that used by T. Shinomiya in that, by the use of two large prisms and a condensing lens L_4 (Fig. 1),

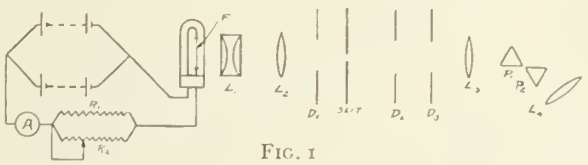

FIG. 1

greater dispersion and better monochromatism were obtained. As the sensitiveness of the photo-electric cell changes in a continuous way along the spectrum, the very slight deviation from the ideal condition of absolute monochromatism had little effect on the final curves.

The set-up is shown diagrammatically in Figure 1. The source of light, F, was a specially constructed tungsten 17-ampere nitrogen-filled lamp made by the Nela Research Laboratory. The bright filament was a straight, narrow flat strip which acted as a line source. A Weston direct-current ammeter, A, measured the current through the lamp. This had to be kept very constant at 17 amperes, for the slightest variation in the intensity of the light made itself felt in both the thermo and photo-electric galvanometers. The current was adjusted by a tin resistance, R_1, and a fine adjustment sliding resistance R_2 in parallel. Two sets of storage batteries connected in parallel served as the source of current. They were kept well charged and the resultant current was steady.

The light was condensed by lenses L_1 and L_2 and brought to a focus on the slit S, which was 0.7 mm in width. It was then rendered parallel by the lens L_3. The diaphragm D_3 was adjusted so that the front face of the prism P_1 was just covered by light. The position of minimum deviation for green-blue light was chosen for both prisms. After passing through the prisms the various

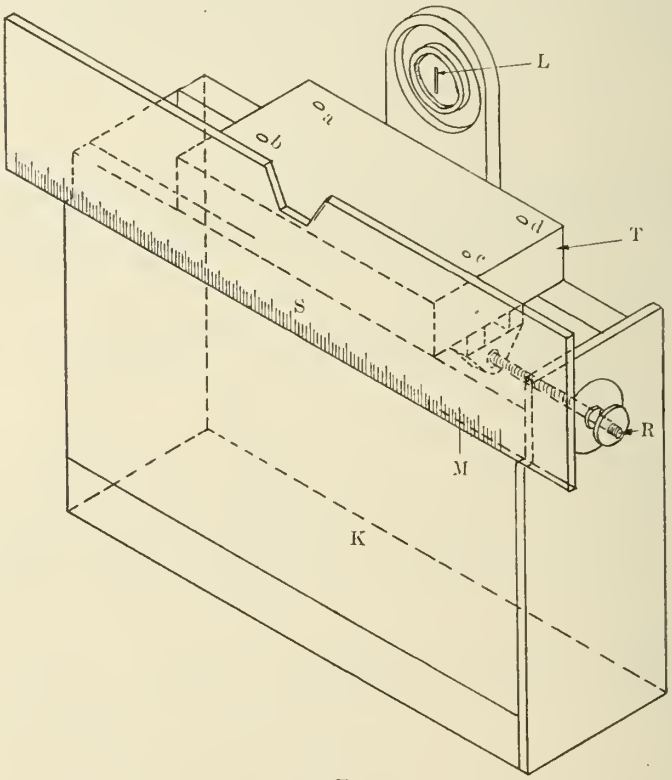

FIG. 2

colors of the spectrum were brought to a focus and made pure by the lens L_4. The spectrum, 10 cm in length, was beautifully distinct and bright. The reflected and stray light was eliminated by the diaphragms D_1, D_2, and D_3, and further by placing the entire optical system in a box made of thin compo-board, completely blackened on the inside. The slit L (Fig. 2) was accurately located

in the focal plane of the lens L_4. It was mounted on the table T, which could be moved through the spectrum by means of the fine screw R. This table was inside a heavy black box K, rigidly attached to a solid pier. The entire optical system was made purposely heavy, so that not even the slightest displacement could take place and hence change the calibrations. One can readily see that a very small change in any part of such a complicated system would throw the whole arrangement out of order. The scale, S, on the outside of the box was rigidly connected with the slit L. It was the sliding of this scale past a fine reference mark M that was calibrated, first in ergs and then in wave-lengths of light.

The mounting for the slit L was made to exactly fit the mounting of the thermo-couple used in the energy calibration. On the top of the table were bored four holes, a, b, c, d (Fig. 2). Into these four holes fit the legs of a light-tight metal box, specially constructed for containing the photo-electric cell under test. The shutter on this box for admitting and cutting off the light to the cells was situated so that it was directly behind the slit L. This shutter was manipulated by the operator at his observing position by means of pulleys and strings. The apparatus was so arranged that at the same place where these strings were situated the operator could adjust the resistance R_2, read the ammeter A, and note the photo-electric galvanometer deflections.

The metal box container had two hard rubber insulators for supporting the photo-electric cell and two insulating plugs and binding posts for the lead wires. The positive lead was made of sulphur, and the negative one of hard rubber. A binding post attached directly to the box served the purpose of grounding the box and the outside of the photo-electric cells.

2. *The photo-electric cells.* There were thirty cells used in the investigation, including all of the alkali metals and the colloida modification of the alkali hydrides of sodium, potassium, rubidium, and cassium. They all contained argon at a low pressure, except two cells where neon was used. Three kinds of glass—common, pyrex, and quartz—were investigated. All of the cells were made

by Dr. Jakob Kunz in this laboratory. A full description of their construction, with the exception of lithium, has been given.[1]

The making of the lithium cell was somewhat of a task, because of the danger encountered in trying to distil lithium, and of the difficulty in obtaining a solute for it. At the suggestion of Dr. A. G. Loomis, of the chemistry department, we tried dissolving it in aethylamine, and were eventually successful. The necessary condition for its solution is that the aethylamine be absolutely dry and that it be in the presence of a trace of ammonia.

The aethylamine was made according to the following directions, the chemical reaction being

$$(C_2H_5NH_2+HBr)+NaOH=NaBr+C_2H_5NH_2+H_2O.$$

Seventy grams of aethylamine hydrobromide were placed in a 500-cc pyrex glass flask, fitted with a tight cork stopper holding a separatory funnel and a reflux condenser kept at about 30° C. To the top of the reflux condenser was attached a drying column of solid NaOH, and this connected to a downward condenser of the spiral type, cooled with ice and salt. The receiver was also cooled with a mixture of crushed ice and salt and had a NaOH tube attached. All stoppers were of cork to prevent the product from becoming yellow because of attack of rubber by the amine.

About 200 grams of a 30 per cent solution of NaOH was slowly dropped into the flask through the separatory funnel, and when all had been added, the mixture was first heated with warm water and later with a flame, refluxing until no more amine condensed into the receiver. The crude amine was then redistilled three or four times, using metallic lithium as a drying agent. The final product was a pure, colorless, dry fluid. Metallic lithium was put into it, in a vessel connected with a cell. After standing ten hours in the aethylamine in the presence of a trace of ammonia, the lithium was dissolved and the clear liquid became a deep-blue color. This solution was poured into the cell and the aethylamine pumped out, leaving a uniformly distributed surface of grayish blue lithium. The cell was then partly filled with argon at low pressure and sealed off.

[1] *Physical Review*, **7**, 62, 1916.

3. *The set-up.* A diagrammatic sketch of the connections is shown in Figure 3. The source of potential E was a set of new dry cells. The voltage ranged anywhere from 100 to 310 volts, depending upon the kind of cell used. The potential was measured by a Weston direct-current voltmeter, V. All of the connecting wires, as well as the battery itself, were insulated by paraffin.

The galvanometer, G, which measured the photo-electric current, was a Leeds and Northrup high-sensitivity type. It had a sensitiveness of 8×10^{-10} amperes for a scale-distance of 1.25 m, and a critical damping resistance of 9600 ohms. To safeguard against short circuit, a resistance of 100,000 ohms was inserted in the

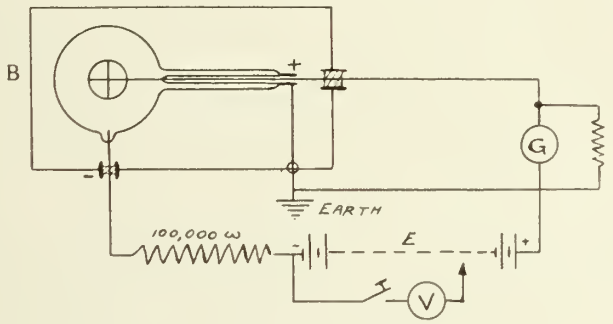

FIG. 3

circuit. The outside of the cell, the positive terminal of the battery, and the box B, Figure 3, containing the photo-electric cell, were all earthed. When working with the lithium cell, a quadrant electrometer had to be used to measure the photo-electric current, because of the small light intensities in the region of its maximum sensitivity, and the rather low sensitiveness of the cell.

4. *Method of procedure.* After the calibrations were made, great care was taken that no part of the system was disturbed. Then a characteristic curve was made of the first cell to be tested, after which a preliminary sensitiveness-curve was run and finally the real sensitiveness-curve data obtained. This procedure was repeated for all the cells used. The process will now be discussed a little more in detail.

The cell was mounted in the box K (Fig. 2), the approximate point of maximum galvanometer deflection was found by referring to the work of T. Shinomiya, and the cell placed at that particular wave-length. Starting with a low voltage, around 80, until a deflection of about 40 mm was obtained, the cell was moved back and forth until the exact maximum was found by trial. Keeping this position, the deflections for varying voltages were noted. The upper limit of the voltage was determined by the unsteadiness of the galvanometer deflections. This unsteadiness indicated that the arcing potential was being reached. If the cell was allowed to glow much, its sensitiveness decreased. A slight glowing oftentimes increased the sensitivity. Glowing could easily be detected by the galvanometer deflections suddenly going off the scale. Whenever this happened, an entirely new characteristic had to be run. The Na and NaH cells were the most difficult to handle, for the characteristic curve rises so rapidly that a variation of 4 volts (one dry cell) often caused great unsteadiness in the deflections, and sometimes glowing. Barring this unsteadiness, the other readings were very steady and could readily be repeated at the time when the data were taken. If, however, a characteristic was run shortly after a cell was made, and again a day or two later, it was found to change somewhat. After a week's time very little change took place. All the data were taken on cells more than a week old. This variation was more marked in the hydrides of the alkali metals than in the pure metals.

Immediately after running a characteristic, the curve was drawn, plotting volts against photo-electric current. Some characteristic curves are shown in Shinomiya's paper.

A constant potential difference was then chosen from the horizontal portion of the curve, or at most up only a short distance on the vertical part. In no case was such a voltage used as to make the galvanometer deflections unsteady, which occurs when the critical potential is approached.

Having selected a safe potential, one that would give reasonably large deflections (100 mm or more), the cell was started at the extreme violet end of the spectrum and by steps of a centimeter was taken up through the red end. This was the preliminary

run to determine approximately the position, not of maximum galvanometer deflection, but of maximum photo-electric sensitiveness. This point varied somewhat from the former and was found by dividing the deflections by the corresponding energy at the given scale-reading. After a lapse of about fifteen minutes, during which time the cell was left in the dark, a second final run was made, again starting at the violet end. If no lapse of time is allowed to take place between the first and second sets of data, the later readings will be higher, because for a short time the cell becomes more sensitive when it has been under the influence of light. Two readings, rarely differing, were taken at each point, and this time they were taken only 3 mm apart in the region of maximum sensitivity. Thus the maximum point was accurately determined to within one $\mu\mu$.

Finally curves were plotted with wave-lengths of light expressed in $\mu\mu$ as abscissae and specific photo-electric sensitiveness as ordinates, the units being 0.61×10^{-11} coulombs per erg.

III. EXPERIMENTAL RESULTS

The question as to how the colloidal modification of the alkali hydrides affect the color-sensitiveness has been studied. It was found that the results of sensitizing by hydrogen were twofold:

a) It shifts the maximum sensitiveness, λ_{max}, to longer wave-lengths by an amount depending upon the alkali used. As can be seen from Table I below, where λ_{max} and the applied voltage of all the cells investigated are listed, NaH shifted 8 $\mu\mu$, KH 16 $\mu\mu$, RbH 8 $\mu\mu$, and CsH gave only the slight change in one $\mu\mu$. Figures 6, 7, and 8 show this shifting graphically.

b) The colloidal modification of the alkali hydrides also increases the sensitiveness; that is, a greater photo-electric current is obtained with a given applied voltage from a hydride cell than from the pure metal. The sensitiveness depends upon the applied voltage, but on the whole the results indicate a larger ordinate for the hydride cells. Pohl and Pringsheim[1] suggest that this increased sensitiveness is due to the greater ease with which the electrons

[1] *Verhandlungen der deutschen physikalischen Gesellschaft*, 13, 211, 1911; 15, 179, 1911.

TABLE I

Type of Cell	λ_{max}	Applied Voltage	Type of Cell	λ_{max}	Applied Voltage
Li	405	246	KH Quartz	462	145
Na 1	419	149	KH Pyrex 1	457	154
Na 2	419	116	KH Pyrex 2	457	127
Mean for Na	419	.....	Rb 1	473	146
			Rb 2	473	123
NaH 1	427	304	Rb 3	473	136
NaH 2	426	182	Rb 4	473	111
NaH 3	427	308	Mean for Rb	473	.....
NaH 4	428	171			
NaH 5	429	140	RbH 1	479	140
Mean for NaH	427	.....	RbH 2	483	101
			RbH 3	481	123
NaH Neon	407	285	Mean for RbH	481	.....
K 1	440	167			
K 2	440	172	RbH Quartz	507	179
Mean for K	440	.....	Cs 1	540	131
			Cs 2	538	117
KH 1	457	119	Mean for Cs	539	.....
KH 2	457	136			
KH 3	454	140	CsH 1	539	148
Mean for KH	456	.....	CsH 2	541	135
			Mean for CsH	540	.....
KH Neon	438	127			

TABLE II

CALIBRATION DATA GIVING THE WAVE-LENGTHS AND ENERGY ALONG THE ARBITRARY SCALE *S*

Scale-Reading	Wave-Length in $\mu\mu$	Energy in Ergs	Scale-Reading	Wave-Length in $\mu\mu$	Energy in Ergs
40.0	393.0	1.53	45.3	456.7	73.8
40.5	397.3	2.04	45.5	462.0	84.4
41.0	401.0	3.84	45.7	466.7	94.3
41.3	403.2	4.59	46.0	473.1	109.1
41.5	404.9	5.89	46.3	483.2	127.3
41.7	406.6	6.55	46.5	488.7	137.9
42.0	409.5	8.68	46.7	496.6	151.5
42.3	412.0	10.48	47.0	506.3	172.0
42.5	414.6	12.56	47.3	516.7	191.9
42.7	416.5	14.67	47.5	524.3	205.7
43.0	419.6	17.35	47.7	535.2	221.0
43.3	423.3	21.22	48.0	550.6	239.0
43.5	425.4	23.58	48.3	567.7	259.2
43.7	428.5	26.85	48.5	580.2	270.1
44.0	433.0	32.70	48.7	593.5	288.2
44.3	438.0	41.30	49.0	616.6	305.3
44.5	440.8	45.20	49.5	660.7	338.5
44.7	445.0	51.75	50.0	718.0	366.7
45.0	451.0	61.80			

can emerge from the tiny globules of metal which characterize the colloidal state.

The curves of color-sensitiveness have been obtained for all the pure alkali metals and for all the hydrides with the exception of Li. The curves resemble resonance curves, and Pohl and Pringsheim have suggested that the selective effect is a molecular resonance phenomenon in which the electron follows the electric force. The curves, however, are not pure resonant ones because of lack of perfect symmetry. If a center line is drawn from the peak of a curve perpendicular to the wave-length axis and then about halfway between the peak and the axis another line is drawn perpendicular to this center line, the distances measured along the latter from the center to the two points where it cuts the curve is a measure of the curve's symmetry. In the pure metal as well as in the hydride of the sodium and potassium cells, the distance from the central line to the right side of the curve was greater than that to the left; Cs and CsH, on the other hand, showed dissymmetry in the opposite direction. The Rb and RbH cells are almost symmetrical. A sufficient number of points are located on each curve so that its exact nature is determined. Many of the points have been omitted from the drawings for the sake of clearness. They all, however, fell upon the smooth curve. An examination of the curves and Table I clearly shows how consistently the cells operated. The position of λ_{max} for individual cells of the same metal fell in almost exactly the same position.

Figures 6 and 7 show how the gas in the cells affects the photo-electric effect. A sodium cell and a potassium cell, each filled with neon instead of the argon of the other cells, showed a decided shift of the λ_{max} toward shorter wave-lengths. The amount of shift was 20 $\mu\mu$ for sodium and 18 $\mu\mu$ for potassium. That there should be such a difference between the λ_{max} for the cells filled with neon and with argon, both being inert gases, is a rather surprising phenomenon. It is probably connected with the fact that the maximum sensitiveness of sodium and potassium in these cells deviates considerably from the values obtained for pure metals without gas. This question requires further study.

Figures 6 and 7 indicate the effect that the kind of glass used in the photo-electric cell has on the wave-length of maximum sensitiveness. Most of the cells were made of common glass, but two cells of pyrex (KH Pyrex 1 and KH Pyrex 2) and two of quartz (KH Quartz and RbH Quartz) were constructed. Both pyrex cells

TABLE III

VARIATION IN ALL ALKALI METALS*

SCALE IN CENTIMETERS	Li		Na 2		K 2		Rb 3		Cs 2	
	Electrical Deflection	Deflection Energy	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness
	mm		mm		mm		mm		mm	
40.0	14.8	1265.0	1.2	62.2	.....	.....	.....	.....	.....	.....
41.0	43.8	1194.0	4.8	99.8	2.0	41.7	0.7	14.6	.....	.....
41.5	70.7	1574.0	8.9	120.9	3.4	46.2	.....	.....	.....	.....
42.0	101.2	1527.0	16.1	148.1	6.6	60.7	2.0	18.4	1.8	16.6
42.3	.....	.....	21.4	163.2	.....	.....	.....	.....	.....	.....
42.5	133.3	1390.0	26.1	166.2	11.9	75.8	.....	.....	.....	.....
43.0	166.5	1256.0	36.6	168.5	21.2	97.6	6.1	28.1	3.9	17.9
43.5	.....	.....	48.3	163.6	36.8	124.7	.....	.....	.....	.....
44.0	.....	.....	57.0	139.2	55.8	136.4	20.2	49.4	9.0	22.0
44.3	.....	.....	60.4	116.9	.....	.....	.....	.....	.....	.....
44.5	302.5	877.0	.....	.....	78.6	139.0	33.5	59.21	.....	.....
44.7	.....	.....	56.8	87.8	88.7	137.0	.....	.....	.....	.....
45.0	321.7	681.5	53.3	68.9	96.7	124.9	.....	.....	21.3	27.51
45.3	.....	.....	.....	.....	107.2	116.1	73.0	79.0	.....	.....
45.5	307.0	476.8	51.0	47.5	113.3	107.4	86.5	81.9	32.9	31.2
45.7	.....	.....	.....	.....	113.3	96.0	101.3	85.8	.....	.....
46.0	250.0	299.7	48.7	35.6	111.4	81.6	120.8	88.6	47.4	34.7
46.3	.....	.....	.....	.....	103.7	63.2	140.4	85.0	.....	.....
46.5	.....	.....	44.8	25.9	93.9	54.4	.....	.....	69.7	40.4
46.7	.....	.....	.....	.....	81.1	42.8	139.7	73.6	.....	.....
47.0	104.7	79.8	41.5	19.3	57.9	27.0	139.0	64.7	104.7	48.7
47.3	.....	.....	.....	.....	33.2	13.9	.....	.....	123.9	51.6
47.5	.....	.....	36.6	14.2	21.2	8.3	123.3	47.9	145.0	56.4
47.7	.....	.....	.....	.....	.....	.....	.....	.....	166.2	60.1
48.0	21.5	11.8	31.0	10.4	6.9	2.3	59.0	19.7	169.0	56.6
48.3	.....	.....	.....	.....	.....	.....	.....	.....	144.2	44.5
48.5	.....	.....	18.8	5.6	3.4	1.0	17.8	52.5	117.2	34.7
48.7	.....	.....	.....	.....	.....	.....	.....	.....	94.7	26.2
49.0	8.0	3.4	10.7	3.1	2.0	0.6	8.4	3.0	48.2	12.6
49.5	.....	.....	7.8	1.8	1.2	0.3	4.3	1.0	11.1	2.6
50.0	4.8	1.7	.....	.....	1.1	0.2	2.1	0.5	3.8	0.9

* The sensitiveness column in each case but Li is multiplied by 10^{-11}, giving the specific photo-electric sensitiveness in coulombs per erg.

gave excellent curves, whose λ_{max} varied only one $\mu\mu$ from that of KH cells made from common glass. The two cells constructed of quartz, however, showed a definite shift in λ_{max} toward longer wave-lengths, by an amount equal to 6 $\mu\mu$ for the KH quartz and 26 $\mu\mu$ for the RbH quartz cell. If this shift due to the quartz was caused by absorption of light in the wall of the cell, one should expect it to be in the opposite direction.

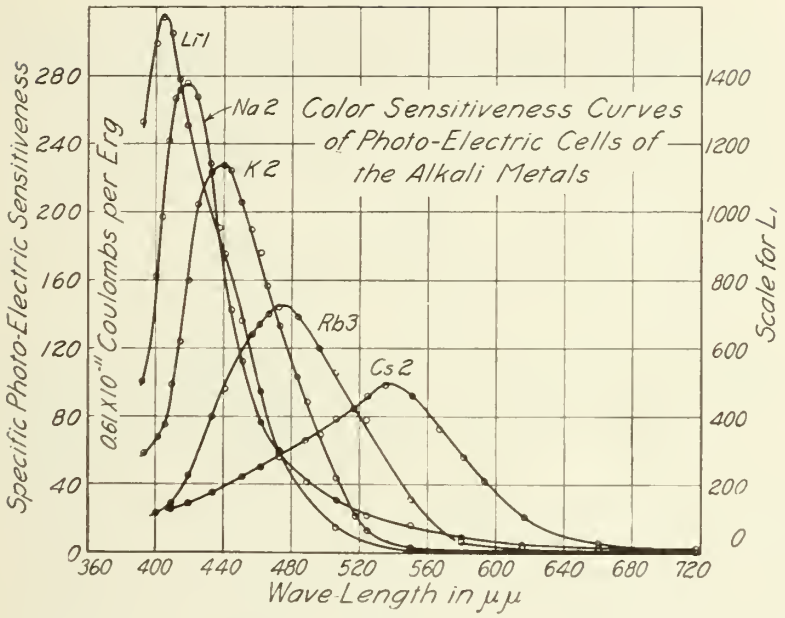
Color Sensitiveness Curves
of Photo-Electric Cells of
the Alkali Metals
Li1
Na2
K2
Rb3
Cs2
Specific Photo-Electric Sensitiveness
.061 X 10⁻¹¹ Coulombs per Erg
Scale for Li
Wave-Length in μμ
0
40
80
120
160
200
240
280
0
200
400
600
800
1000
1200
1400
360
400
440
480
520
560
600
640
680
720

FIG. 4a

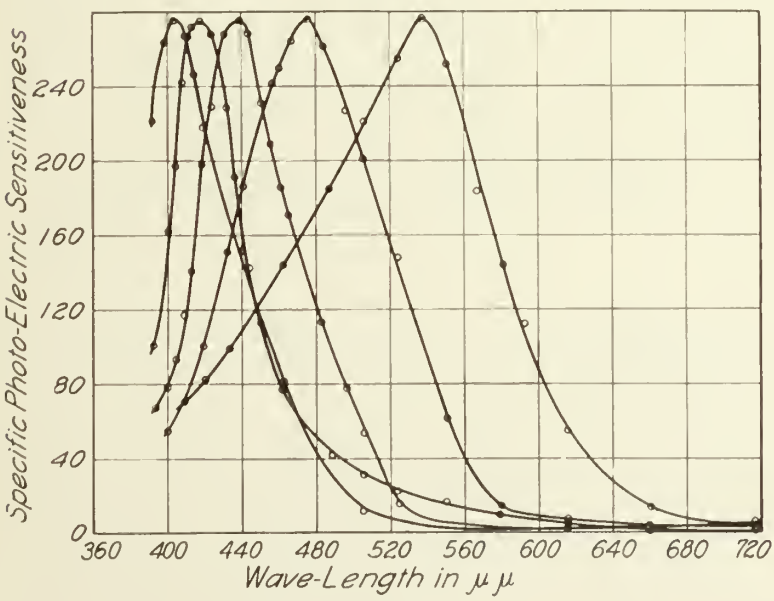
Specific Photo-Electric Sensitiveness
Wave-Length in μμ
0
40
80
120
160
200
240
360
400
440
480
520
560
600
640
680
720

FIG. 4b

A further experiment was carried on for the purpose of detecting a fatigue effect in a K and a KH cell. The temperature, intensity of light, and applied voltage were kept constant and the galvanometer deflections observed at intervals of from ten to twenty-four hours. The voltage continuously applied to the K cell was 110 and after

TABLE IV

VARIATIONS IN THE HYDRIDE CELLS*

SCALE IN CENTIMETERS	NaH 1		KH 1		RbH 2		CsH 2	
	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness
	mm		mm		mm		mm	
40.0	5.8	302.2						
41.0	15.9	331.1	2.5	52.0	1.1	22.9		
41.5	26.8	364.2	3.9	53.0				
41.7	32.3	394.0						
42.0			6.4	58.7	2.8	25.7	1.1	10.1
42.3	59.0	449.5						
42.5			10.5	70.0				
43.0	108.3	500.2	17.5	80.6	7.3	33.6	2.3	10.6
43.5	152.5	516.6	30.0	101.7				
44.0	203.0	496.0	50.0	122.0	23.5	57.4	11.9	12.0
44.5	195.5	345.9	81.2	143.7	38.7	68.4		
44.7			98.7	152.4				
45.0	183.0	236.4	127.3	164.5	62.9	81.2	13.0	16.8
45.3			155.7	168.6	81.9	88.6		
45.5	161.6	153.2	172.4	163.4	97.0	91.9	21.0	19.9
45.7					113.5	96.2		
46.0	134.5	98.3	190.2	139.5	137.5	100.8	35.3	25.9
46.3					164.0	102.9		
46.5	107.0	62.0	183.6	107.6	170.6	99.0	57.3	33.2
46.7					174.3	91.9		
47.0	82.2	38.1	161.9	75.2	171.0	79.5	95.3	44.3
47.3							121.5	50.8
47.5	54.5	21.2	126.4	49 1	138.2	53.7	147.1	57.2
47.7							172.4	62.3
48.0	30.3	10.1	85.3	28.5	88.9	29.7	176.4	58.9
48.3							151.7	46.8
48.5	14.0	41.5	45.8	13.6	46.3	13.7	106.5	31.4
48.7							77.7	21.5
49.0	7.0	1.9	20.1	5.3	20.1	5.3	31.6	8.3
49.5	4.6	2.0	10.0	2.4	7.7	1.8	5.6	1.3
50.0	3.3	0.7	7.0	1.5	3.3	0.7	1.7	0.4

* The sensitiveness column in each case is multiplied by 10^{-11}, giving the specific photo-electric sensitiveness in coulombs per erg.

five hundred and twenty-five hours' exposure to strong light the cell had *increased* in sensitiveness by quite a large amount. The galvanometer deflections began with 176 mm and gradually increased up to 300 mm at the end of the exposure. The KH cell, on the other hand, under the same conditions, except that the applied voltage was 36, showed an exceptional constancy. Slight

fluctuations occurred during the one thousand hours' exposure; the initial and final galvanometer deflections were 194 mm and 191 mm, respectively, showing that the fatigue is negligible.

These same two cells were exposed for 60 hours *without* continuously applying a voltage. At the times when the photo-electric galvanometer deflections were taken, a voltage of 100 was applied to the potassium cell and of 27 to the potassium hydride cell. All the conditions remained constant throughout the experi-

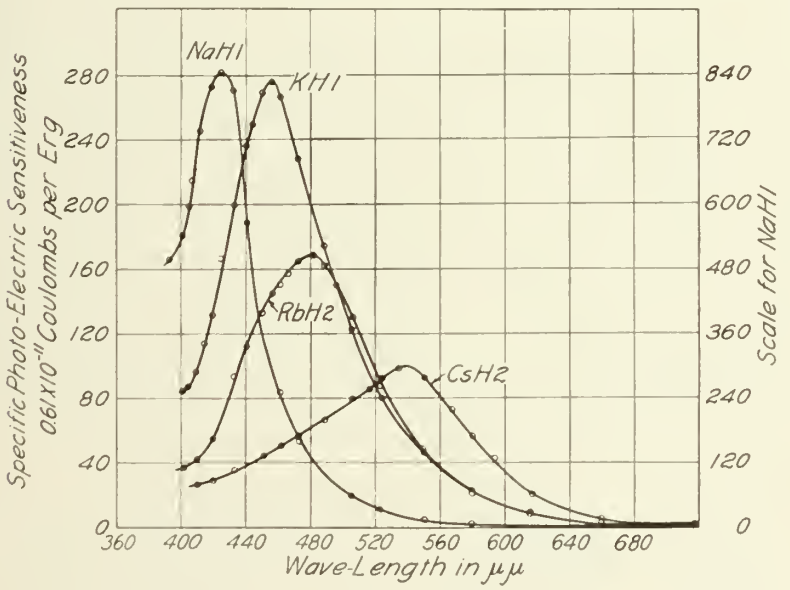

FIG. 5

ment. The results showed an *increase* in sensitiveness for both cells, the initial and final deflections for the potassium cell being 206 mm and 274 mm, and those for the potassium hydride cell being 196 mm and 316 mm. It seems strange that merely the exposure to light, without the passage of a photo-electric current, should increase the sensitiveness so much more rapidly than when the applied voltage caused a current to flow constantly through the cells. Both investigations, however, point to a negative conclusion in regard to a fatigue effect.

TABLE V

VARIATIONS IN POTASSIUM CELLS*

Scale in Centimeters	K 1		KH 2		KH Quartz		KH Pyrex 1		KH Neon	
	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness
	mm		mm		mm		mm		mm	
41.0	3.8	79.0	2.5	52.0	1.0	20.8	1.7	34.7	5.8	120.7
41.5	6.2	84.2	.....	.....	1.6	21.8	.....	.....	9.6	130.4
42.0	9.8	90.2	6.0	55.2	2.6	23.9	9.6	42.2	16.9	148.1
42.5	15.2	96.7	10.0	63.6	4.2	26.7	9.0	57.4	27.2	173.0
43.0	23.5	108.2	16.5	76.0	6.9	31.8	15.1	69.4	44.0	202.6
43.5	36.1	122.4	28.4	96.2	11.8	39.9	32.2	109.3	70.7	239.6
44.0	53.0	129.4	49.0	119.6	20.1	49.0	53.2	130.2	105.0	256.5
44.5	74.3	131.4	80.2	141.8	33.8	59.8	.....	.....	145.3	256.9
44.7	84.1	129.8	98.7	152.4	42.7	66.0	96.6	149.0	161.8	249.8
45.0	98.0	127.4	131.3	169.8	59.8	77.3	122.7	158.5	187.0	241.9
45.3	.....	.....	162.3	175.5	79.4	85.8	154.4	167.0	207.5	224.3
45.5	124.8	118.3	178.0	168.6	92.0	87.2	171.5	162.5	213.0	201.8
45.7	129.5	109.7	.....	.....	102.5	86.8	.....	.....	.....	.....
46.0	128.9	94.4	194.8	142.6	112.8	82.6	200.0	146.4	204.0	149.5
46.3	119.7	75.2	.....	.....	117.0	73.4	.....	.....	.....	.....
46.5	108.5	62.9	177.9	103.0	117.7	68.2	210.5	122.0	170.0	98.5
46.7	93.9	49.5	.....	.....	119.3	62.9	.....	.....	.....	.....
41.0	66.8	31.1	144.8	67.4	120.0	55.8	212.0	98.4	118.0	54.8
47.3	41.0	17.1	.....	.....	116.9	48.7	.....	.....	.....	.....
47.5	27.3	10.6	90.6	32.2	110.7	43.0	184.0	71.5	65.1	25.3
48.0	10.4	3.5	38.3	12.8	72.0	24.0	126.1	42.1	30.0	10.0
48.5	6.7	1.9	14.0	4.2	26.3	7.7	56.2	16.6	14.8	4.4
49.0	5.0	1.3	7.3	1.9	6.1	1.6	20.0	5.2	7.5	2.0
49.5	3.9	0.9	5.2	1.2	1.7	0.4	11.5	2.7	3.5	0.9
50.0	3.0	0.7	4.0	0.9	0.8	0.2	9.4	2.1	1.9	0.4

*The sensitiveness column in each case is multiplied by 10^{-11}, giving the specific photo-electric sensitiveness in coulombs per erg.

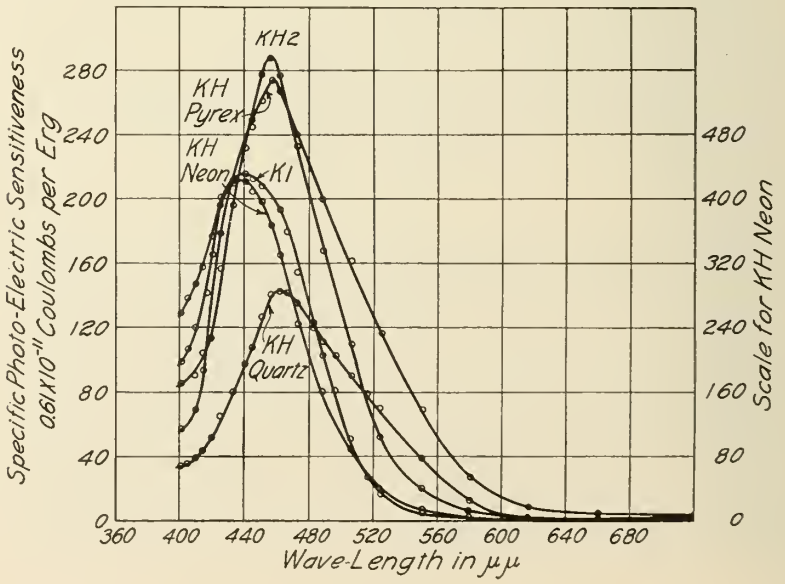

FIG. 6

TABLE VI

VARIATIONS IN SODIUM CELLS*

SCALE IN CENTIMETERS	NA 1		NAH 4		NAH 5		NAH NEON	
	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness
	mm		mm		mm		mm	
40.0	1.2	.....	1.5	78.2	0.9	46.5	2.3	119.9
41.0	8.2	170.5	4.0	83.2	2.9	60.4	6.4	133.3
41.5	16.8	228.3	6.5	88.3	4.9	66.6	10.2	138.7
42.0	29.0	267.1	.....	.....	8.2	75.4	15.2	139.0
42.3	.....	.....	13.4	102.2	.....	.....	17.8	135.7
42.5	46.0	292.6	.....	.....	13.2	84.0	.....	.....
43.0	.....	.....	24.9	114.5	20.1	92.6	27.2	125.3
43.3	.....	.....	31.5	118.5	25.6	96.4	31.5	118.5
43.5	83.8	284.0	36.8	124.7	29.9	101.4	.....	.....
43.7	.....	.....	42.0	124.9	35.0	104.2	.....	.....
44.0	106.0	258.9	49.9	121.8	.....	.....	41.2	100.5
44.3	.....	.....	.....	.....	.....	.....	.....	.....
44.5	125.9	222.4	62.8	111.1	57.1	100.8	48:8	86.2
44.7	134.0	207.1	.....	.....	64.9	96.7	50.0	77.2
45.0	146.9	189.9	76.3	98.6	.....	.....	53.9	69.7
45.3	157.2	170.1	.....	.....	.....	.....	.....	.....
45.5	162.8	154.2	91.2	86.4	97.2	81.2	.....	.....
46.0	165.0	120.8	100.0.	73.4	.....	.....	58.0	42.5
46.5	148.1	85.8	96.0	55.6	96.0	55.5	.....	.....
47	107.3	49.8	71.8	33.4	79.8	37.1	45.2	21.0
47.5	.....	.....	34.3	13.4	.....	.....	29.9	11.7
48.0	18.2	6.1	11.3	37.8	21.0	.....	13.2	4.4
48.5	9.2	2.8	.....	.....	.....	.....	.....	.....
49.0	6.4	1.7	2.6	0 7	0.8	0 2	1.1	0.3
49.5	4.5	1.0	.....	.....	.....	.....	.....	.....
50.0	3.0	0.7	1.5	0.3	.....	.....	0.3	0.1

* The sensitiveness column in each case is multiplied by 10^{-11}, giving the specific photo-electric sensitiveness in coulombs per erg.

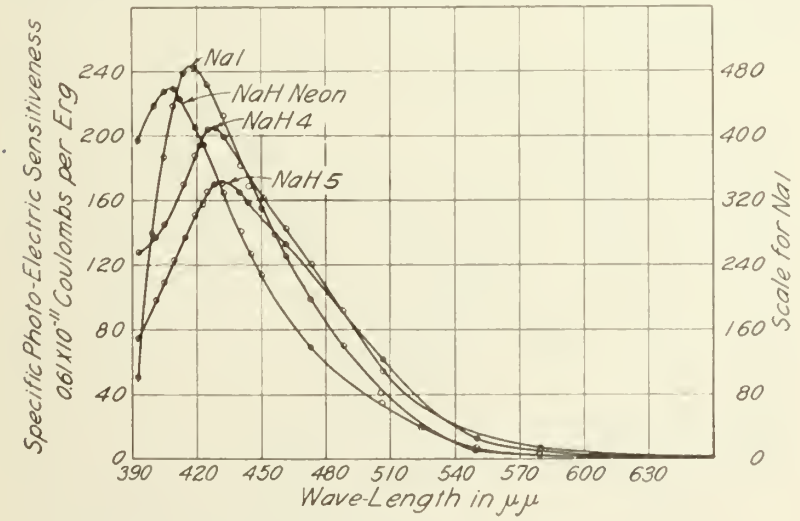

FIG. 7

TABLE VII

VARIATION IN RUBIDIUM AND CAESIUM CELLS*

SCALE IN CENTIMETERS	Rb 2		RbH 3		RbH Q		Cs 1		Cs H 1	
	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness	Galvanometer Deflections	Specific Photo-Electric Sensitiveness
	mm		mm		mm		mm		mm	
41.0	1.0	20.8	.....	.....	0.5	10.7	.....	.....	.....	.....
41.5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
42.0	2.8	25.7	5.3	30.4	1.2	11.0	0.7	6.3	1.0	9.2
42.3	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
42.5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
42.7	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
43.0	7.8	35.9	7.2	33.1	2.6	12.0	1.5	6.9	2.1	9.7
43.3	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
43.5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
43.7	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
44.0	22.3	54.5	18.8	45.9	6.1	14.9	3.4	8.3	6.9	16.8
44.3	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
44.5	35.0	61.9	29.9	52.3	10.5	18.6	.....	.....	.....	.....
44.7	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
45.0	55.5	71.8	50.0	64.6	18.3	23.7	8.6	11.1	20.1	26.0
45.3	72.8	78.8	67.2	72.8	25.5	27.6	.....	.....	.....	.....
45.5	85.5	81.0	80.9	76.6	31.8	30.1	14.7	13.9	31.6	30.0
45.7	99.6	84.4	97.9	83.0	41.4	35.8	.....	.....	.....	.....
46.0	119.0	87.2	122.1	89.5	51.2	41.2	24.8	18.2	48.7	35.7
46.3	134.5	84.4	145.5	91.3	77.2	48.5	.....	.....	.....	.....
46.5	138.3	80.1	155.9	90.4	91.6	53.1	41.0	23.7	71.6	41.5
46.7	138.6	73.2	162.0	85.4	110.6	58.3	51.2	27.0	84.1	44.4
47.0	126.6	58.2	157.9	73.4	131.8	61.2	69.8	32.5	106.0	49.3
47.3	.....	....8..	.....	.....	144.0	59.9	90.0	37.5	126.5	52.6
47.5	84.4	32..	117.0	45.5	146.2	56.8	108.7	42.2	150.4	59.0
47.7	.....	....8..	.....	.....	147.7	53.4	126.2	45.6	171.5	62.0
48.0	40.5	13..	63.4	21.2	129.3	43.3	132.1	44.2	171.0	57.2
48.3	.....	....6..	.....	.....	.....	.....	122.5	37.8	147.6	45.5
48.5	17.0	5..	27.7	8.2	87.1	25.7	93.8	27.7	103.9	30.7
48.7	.....	....0..	.....	.....	.....	.....	.....	.....	75.8	21.1
49.0	6.1	1..	12.4	3.2	48.5	12.7	36.5	95.8	29.0	7.7
49.5	2.1	0.6	6.0	1.4	25.9	6.1	6.8	1.6	4.3	1.0
50.0	0.9	0.5	4.1	0.9	8.9	2.3	2.8	0.6	1.3	0.3

*The sensitiveness column in each case is multiplied by 10^{-11}, giving the specific photo-electric sensitiveness in coulombs per erg.

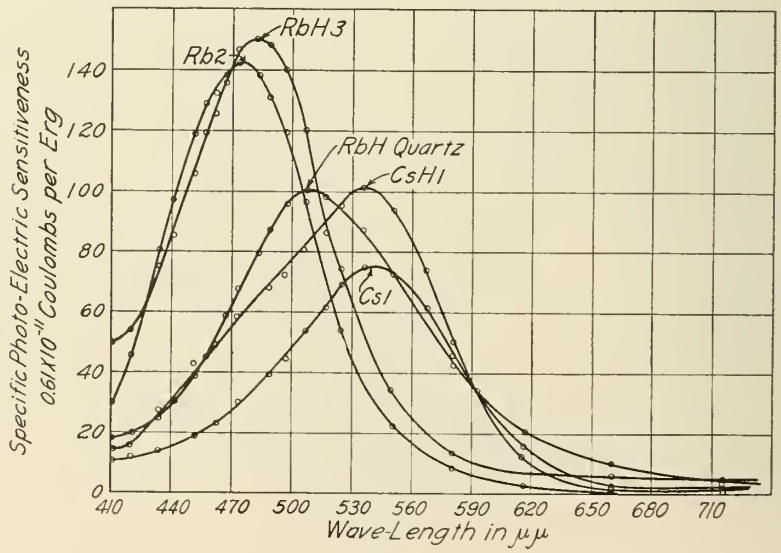

FIG. 8

IV. THEORETICAL CONSIDERATIONS

The results here obtained cannot be used directly for theoretical considerations, because of the effect which absorption of light in the glass wall and the presence of gas in the cell have upon them. Moreover, these results are due to both the normal and the selective effects, for they have not been separated in the present study. Conclusions which have been drawn from previous results are only approximately true. Certain equations to follow, are deduced from theoretical considerations, and when the values from this study are substituted in them, the results show a coincidence of about the same degree of approximation as those previously obtained.

Since the curves resemble resonance curves, it is natural to assume that the frequency $n_{ph} = \frac{1}{\lambda_{max}}$, at which the maximum sensitiveness takes place, is connected with the resonance potential and the resonance frequency of the alkali vapors, where the quantum relation $V_r e = hn_r$ and $V_i e = hn_i$ holds for resonance and ionization potentials respectively. All photo-electric phenomena seem to be governed by the quantum relation, so that one might expect proportionality between hn_{ph} and hn_r or hn_i. Thus proportionality may exist between n_{ph} and the resonance and ionization potentials, i.e., the ratios $\frac{n_{ph}}{V_i}$ and $\frac{n_{ph}}{V_r}$ may be constants. These values are calculated both from the λ_{max} found in Pohl and Pringsheim[1] and from this study, and are given in Table VIII.

A glance will show that the latter values are more nearly constant, in spite of the fact that the values of λ_{max} for Na and Li are greatly at variance with the former. In this work they were found to be in the visible spectrum and others have located them in the ultra-violet region. The ionization and resonance potentials are those determined by Tate and Foote for alkali vapors. The greatest variation from constancy in these ratios is in the case of $\frac{n_{ph}}{V_r}$ for Na. It seems probable that the value of V_r for Na is a little high. Why should it be higher than that for Li, for V_i and V_r both seem to decrease as the atomic weight increases with this one exception?

[1] *Die lichtelektrischen Erscheinungen*, p. 33, Table IX.

It was thought that possibly the product of λ_{max} and the melting-point temperature T_m of the alkali metals (Wien's law) might be constant. This calculation shown in Table IX gives fairly good values for the constant C.

The results as graphed in Figures 4 and 5 show clearly that as the atomic weight of the alkali metal decreases, (*a*) the position of λ_{max} shifts toward the violet, (*b*) the sensitiveness in general

TABLE VIII

Metal	Ionization Potential V_i	Resonance Potential V_r	λ_{max}	Frequency n_{ph}	$\frac{n_{ph}}{V_i}$	$\frac{n_{ph}}{V_r}$
Li	5.36	1.84	280	10.68	1.99	5.80
Na	5.11	2.09	340	8.81	1.72	4.21
K	4.32	1.60	435	6.88	1.59	4.30
Rb	4.16	1.55	480	6.23	1.50	4.02
	VALUES OF $\frac{n_{ph}}{V_i}$ AND $\frac{n_{ph}}{V_r}$ FROM THIS INVESTIGATION					
Li	5.36	1.84	405	7.41	1.38	4.03
Na	5.11	2.09	419	7.16	1.40	3.43
K	4.32	1.60	440	6.82	1.58	4.26
Rb	4.16	1.55	473	6.34	1.52	4.09
Cs	3.88	1.45	539	5.56	1.43	3.83

TABLE IX

Element	λ_{max}	T_m	$C \times 10^5$
Li	405	458.0	1.86
Na	419	370.5	1.55
K	440	335.3	1.48
Rb	473	311.0	1.47
Cs	539	299.0	1.61

increases, (*c*) the resonant point, if such it may be called, becomes more marked, that is, the lithium curve is narrower than that of Cs. In order to show this latter point, an extra Figure 4*b* has been made, where the curves are so drawn that the maximum ordinates are all equal.

In regard to the shifting of λ_{max} as we go from Cs to Li, it is known that a similar relation holds for the "convergence frequency" of the principal spectral series for these alkali metals.

It may be connected with the increase in atomic volume. The colloidal state increased the volume and shifted λ_{max} toward longer wave-lengths, so it is natural to suppose that a large atomic volume means that the electron is held less firmly and consequently can be set in motion by a quantum of relatively small magnitude—that is, at a longer wave-length—than in the case of a substance with small atomic volume. Therefore Cs, having an atomic volume five times larger than Li, would have a λ_{max} of a much longer wave-length.

Two formulas, 1 and 2, have been suggested by Lindemann[1] which are partly of an empirical character.

$$n_{ph} = \frac{e}{2\pi}\sqrt{\frac{n_v}{mr^3}} \quad \text{or}$$

$$n_{ph} = \frac{e}{2\pi}\sqrt{\frac{dn_v}{mM}} \qquad (1)$$

where n_{ph} is the characteristic violet frequency or the maximum color-sensitiveness frequency, e the charge on the electron in electrostatic units, n_v the valency, m the mass of the electron, r one-half the distance between the centers of two neighboring

TABLE X

Element	d	Atomic Weight	$M \times 10^{-24}$ grams	$n_{ph} \times 10^{-15}$	λ_{max} Calculated	λ_{max} Observed
Li	0.51	6.94	11.17	1.276	235	405
Na	0.97	23.00	37.09	0.991	303	419
K	0.86	39.10	63.02	0.771	390	440
Rb	1.52	85.45	137.60	0.642	467	473
Cs	1.88	132.81	214.20	0.574	523	539

atoms, d the density, and M the atomic mass. Table X shows the comparison between the observed λ_{max} and those calculated from Formula 1.

The second formula is a combination of Haber's unexplained equation $n_{ph} = n_r\sqrt{M/m}$, where n_r is the characteristic red frequency

[1] *Berichte deutschen physikalischen Gesellschaft*, 13, 1107, 1911.

emitted by the vibrating atom, and Lindemann's melting-point equation:

$$n_r = \frac{1\sqrt{3k}}{2\pi\left(\frac{3}{4\pi}\right)^{\frac{1}{3}}} \sqrt{\frac{T_m}{MV^{\frac{2}{3}}}}.$$

Substituting the latter in the former, we get

$$n_{ph} = \frac{K1\sqrt{T_m}}{\sqrt[3]{V}} \qquad (2)$$

where K is a constant and V is atomic volume. A calculation of n_{ph} from Formula 2 shows that the agreement between theory and experiment is unsatisfactory.

V. SUMMARY AND CONCLUSIONS

Experimental results show:

1. That due to the formation of a hydride there is a shifting of the point of maximum color-sensitiveness (λ_{max}) toward longer wave-lengths for all the alkali metals.

2. That due to an increase in the atomic volume λ_{max} shifts toward longer wave-lengths as we go from Li to Cs.

3. That the curves of color-sensitiveness become broader with increase in atomic weight.

4. The curves of color-sensitiveness for the entire alkali group have been completed.

5. That the effect of making photo-electric cells of quartz is to cause the position of λ_{max} to shift toward longer wave-lengths. This is contrary to what one would expect.

6. That the presence of neon instead of argon in the cells of Na and K shifts λ_{max} toward shorter wave-lengths.

7. That no fatigue effect can be detected.

Theoretical results show:

1. The approximate constancy of the product of the wave-length of maximum sensitiveness and the ionization potential for both the pure metals and the hydrides.

2. The approximate constancy of the product of the wave-length of maximum sensitiveness and the melting temperatures.

3. A fair agreement between observed values of λ_{max} and those calculated from Formula 1 of Lindemann.

4. That the agreement between theory and experiment in Formula 2 of Haber and Lindemann is unsatisfactory.

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